"Synthesis, Processing, and Properties of $TaC-TaB_2-C$ Ceramics"

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NSWCCD

Sub-Micron and Nanostructured Ceramics

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Background

- TaC and TaB_2 with melting temperatures of 3980°C and 3037°C, respectively, are candidates for ultra-high temperature applications, such as propulsion systems and hypersonic vehicles. There are very limited data on the preparation and properties of ceramics containing both TaC and TaB_2.
- TaB_2-TaC system has a eutectic at 2730˚C at 34 wt.% TaC and no component solubility below 2100˚C.
- Intermediate composition ceramics in the TaC-TaB_2 system had higher hardness and lower wear at 800 - 900 ˚C than the end members.
- Densification of TaC requires temperatures up to 2400°C and TaB_2 – 2100-2200 ˚C.
- Densification temperature of TaC was decreased to 2100-2200˚C by the addition of 10 wt. % fine TaB_2 and B_4C/C mixture (0.43/0.13 wt.%).
- The reactions of transition metals, carbides, and oxides with B_4C are well known and used for synthesis of diboride-based ceramics.
- Pressureless sintering of fine B_4C to relative density above 95% at 2100-2250°C was accomplished by the addition of Group IV-VI transition metal carbides.
- Diborides and active carbon formed during processing accelerated diffusion in the bulk and along grain boundaries. *Me*B_2 had a grain-growth-inhibiting effect.

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Objective:

- Synthesize ceramic materials in the system TaC – TaB_2 – C using displacement reactions between sub-micron TaC and B_4C
- Develop processing procedure for materials densification
- Characterize the microstructure and properties of ceramics

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Reactions in $TaC+B_4C$ Mixtures and Composition of the Reaction Products (in volume fractions)

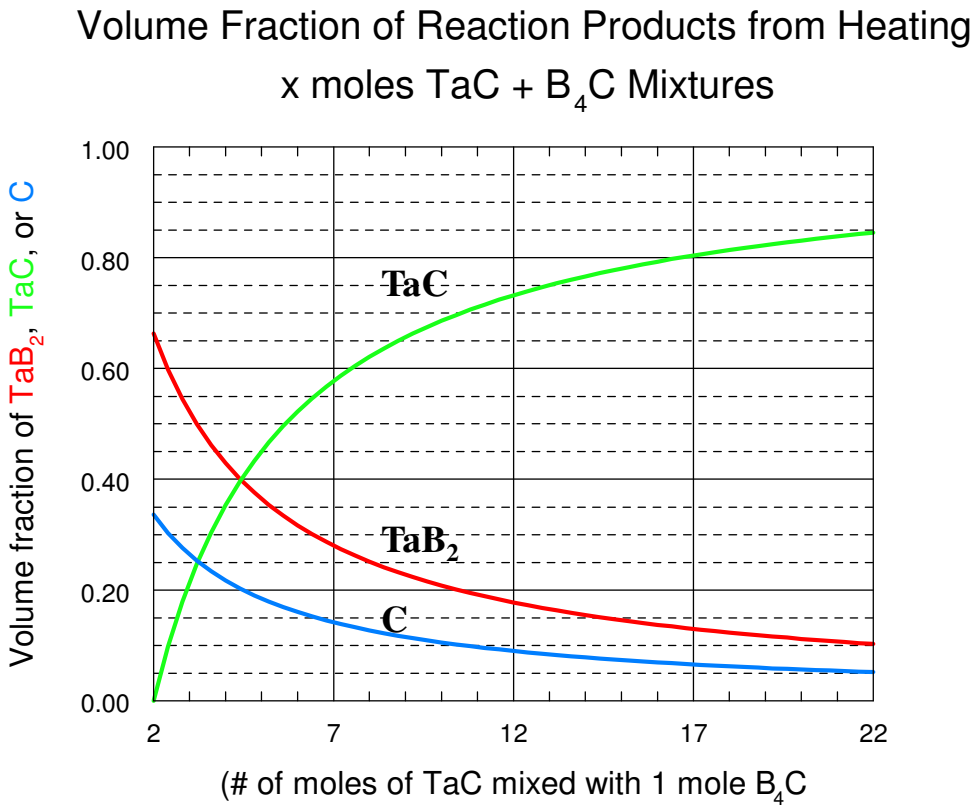
$2TaC+B_4C \Rightarrow 2TaB_2 +3C$

$4TaC+ B_4C \Rightarrow 2TaC+ 2TaB_2 +3C$

$8TaC+ B_4C \Rightarrow 6TaC+ 2TaB_2 +3C$

$12TaC+ B_4C \Rightarrow 10TaC+ 2TaB_2 +3C$

$16TaC+ B_4C \Rightarrow 14TaC+ 2TaB_2+3C$



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Composition of Starting and Reaction Product Components

TaC/B_4C Ratio	Wt% B_4C in raw materials	Calculated Volume% of Reaction Products			Calculated Wt% of Reaction Products		
		TaC	TaB_2	C	TaC	TaB_2	C
2	12.5	0	67	33	0	91.8	8.2
4	6.65	35	42.5	22.5	46.6	49.0	4.4
8	3.45	62	25	13	72.4	25.3	2.2
12	2.3	73.8	17.6	8.6	81.4	17.1	1.5
16	1.75	79.9	13.4	6.7	85.9	12.9	1.15

Actual carbon content in ceramics was lower. It was consumed by oxygen (3.02 wt.%) present in starting TaC during firing.

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Starting Materials

TaC - 99.9% pure, 100 nm, **made in 1976** by Atomergic Chemetals Corp., which does not make it any more.

Stoichiometry - $TaC_{0.96}$ (Chemical and XRD analysis). Oxygen content – 3.02 wt. % (Laboratory Testing Inc., Hatfield, PA).
Surface area - 11.74 m^2/g (NSWCCD by BET).

W was not detected by EDS or XPS. The presence of Cl and H-C bonds was determined by XPS.

It can be assumed that the powder was prepared by gas phase deposition using Ta chloride/hydrocarbon mixtures.

TaC - 99.5% pure; -325 mesh, CERAC Inc. Surface area - 1.02 m^2/g

B_4C - 99.4% pure (metals basis), 1-7 Micron powder, Alfa Aesar
Surface area - 4.84 m^2/g.
C black – surface area about 25 m^2/g

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Experimental Procedure

- Mixing the components in selected molar ratios.
- Sample preparation by cold pressing and following CIPing.
- Heating in the furnace with graphite heaters at 1500 –2100°C for 2 hours in Ar.
- Hot Pressing at 1700 and 1900ºC and 20 MPa for 1hr in He.
- Characterization:
  - Phase composition by XRD
  - Microstructure by SEM
  - Vickers hardness (Load - 1kg and 10kg for 15 seconds)
  - Flexural strength (3-point)

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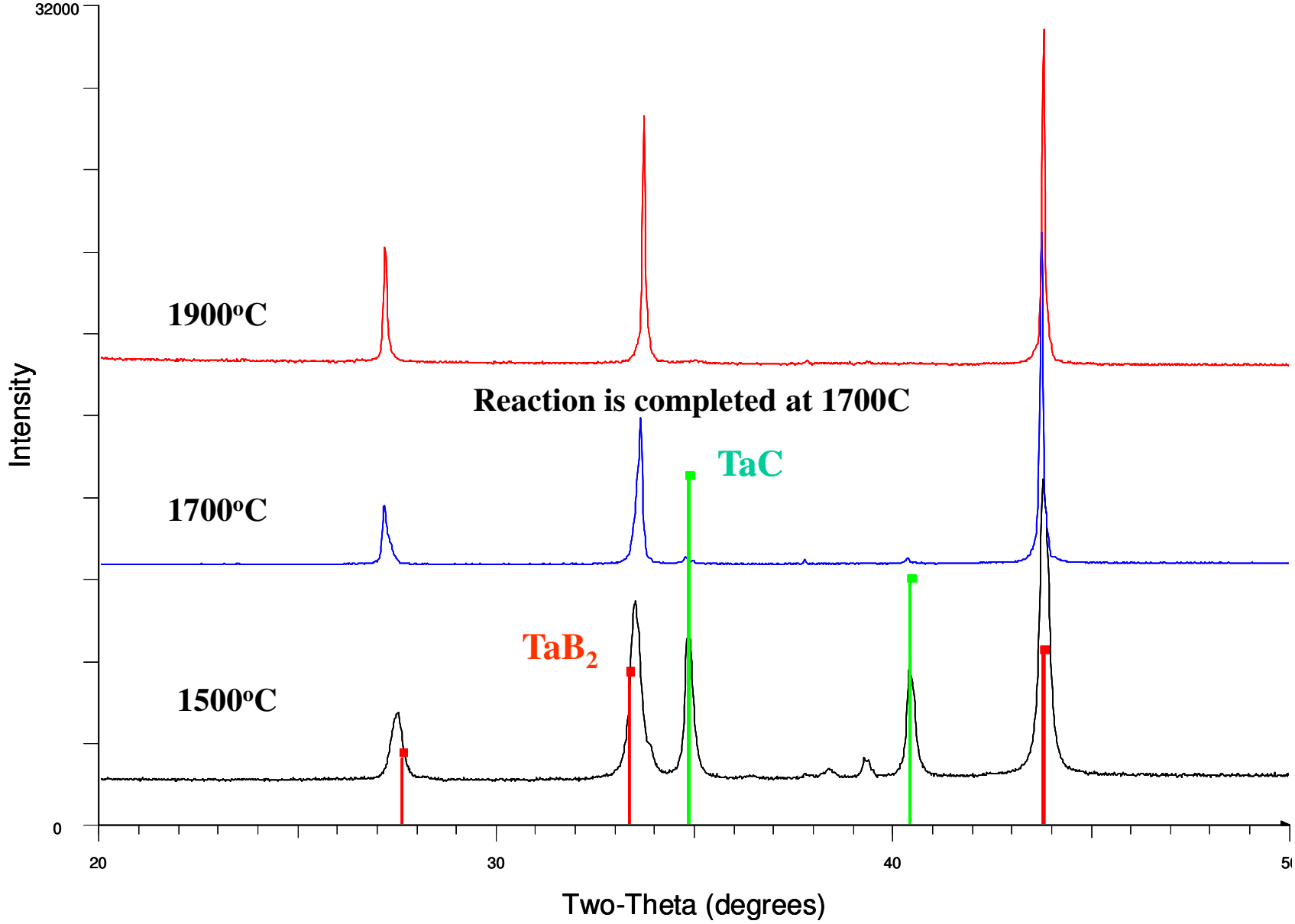
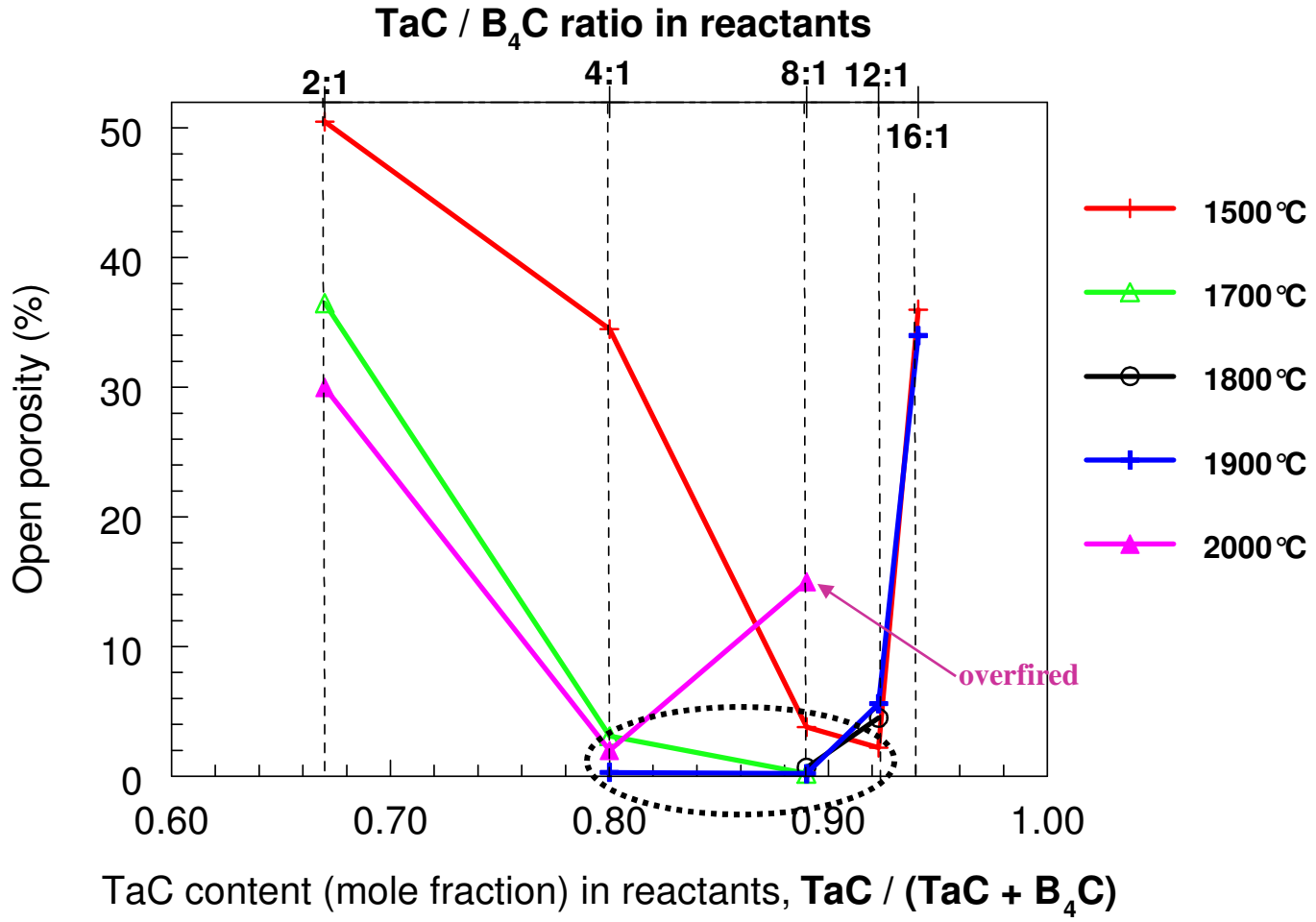
XRD of Ceramics Prepared from $2TaC+B_4C$ Mixture by Pressureless Sintering at 1500, 1700, and 1900°C for 2 hours in He



Open Porosity of Ceramics Prepared from TaC/B_4C Mixtures by Pressureless Sintering as a Function of Composition and Temperature



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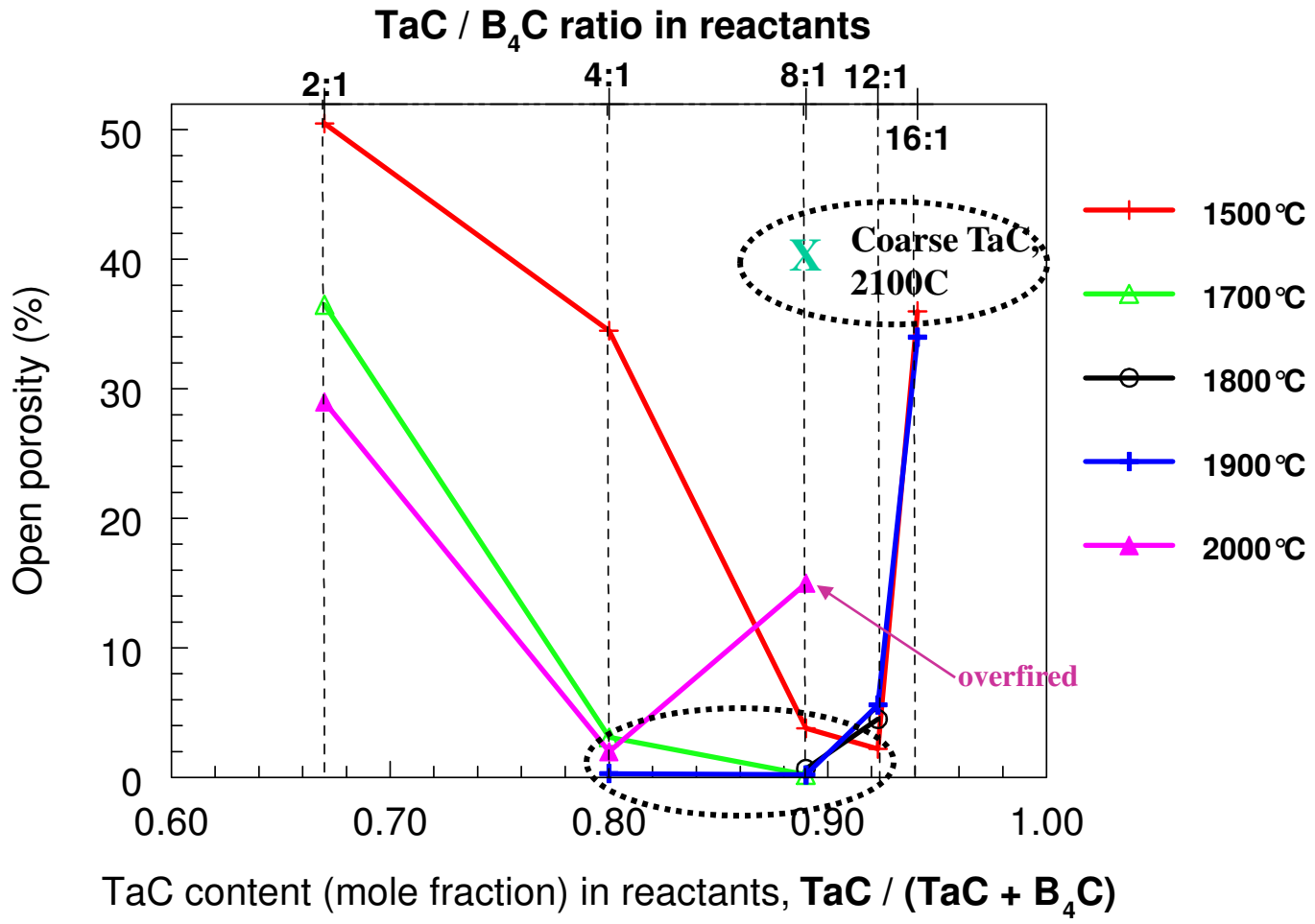
Open Porosity of Ceramics Prepared from TaC/B_4C Mixtures by Pressureless Sintering as a Function of Composition and Temperature



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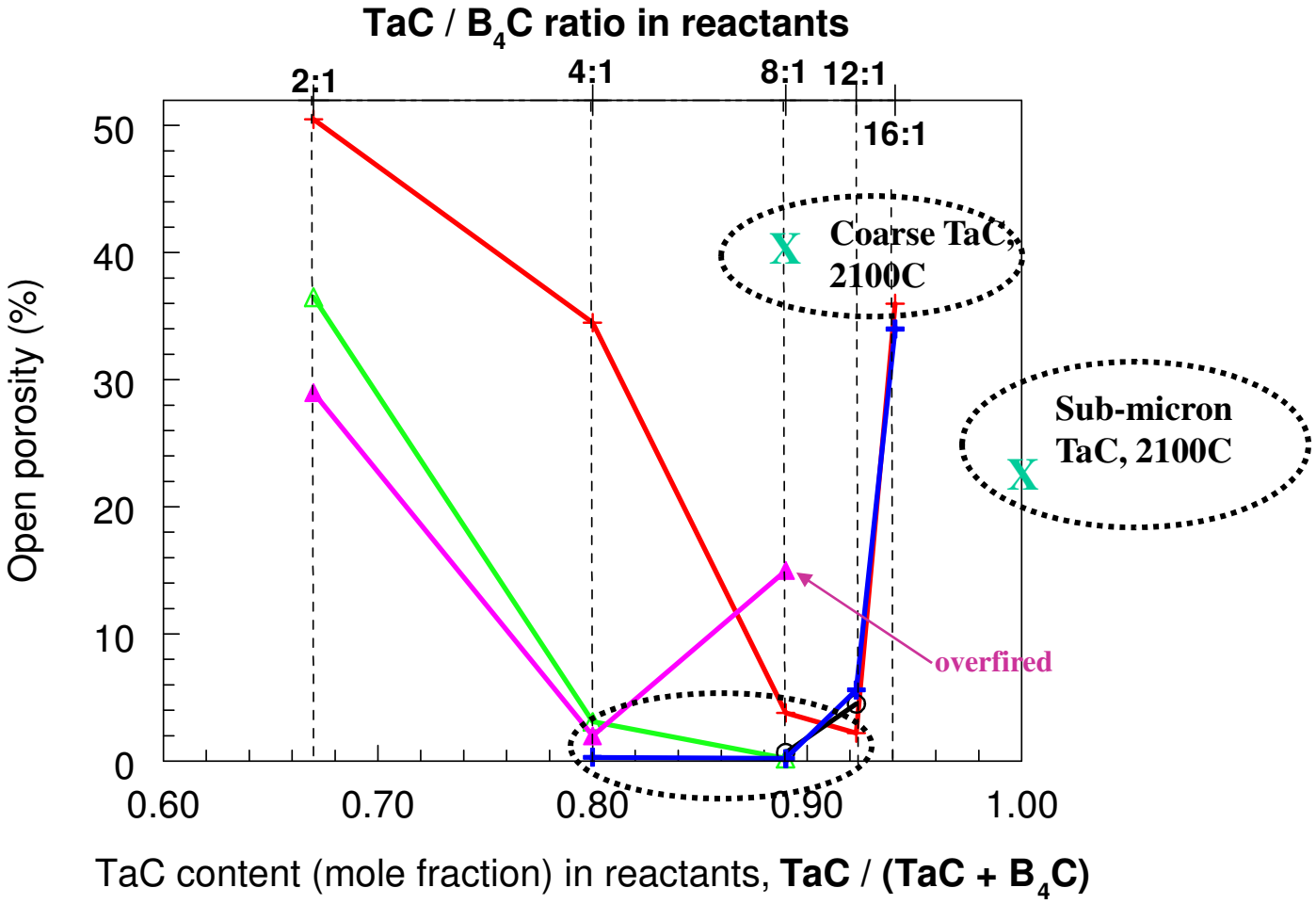
Open Porosity of Ceramics Prepared from TaC/B_4C Mixtures by Pressureless Sintering as a Function of Composition and Temperature



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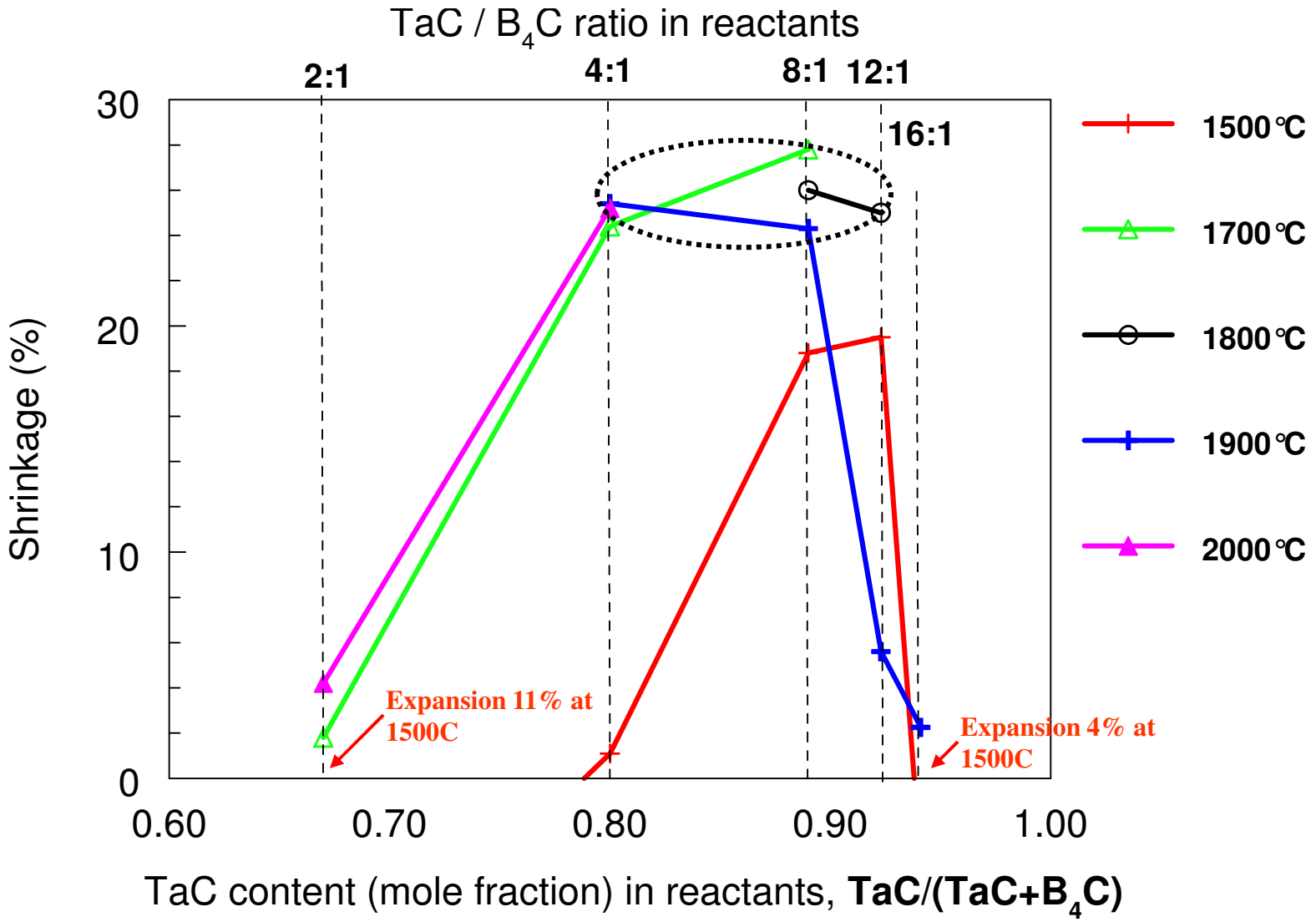
Shrinkage of Ceramics Prepared from TaC/B_4C Mixtures by Pressureless Sintering as a Function of Composition and Temperature



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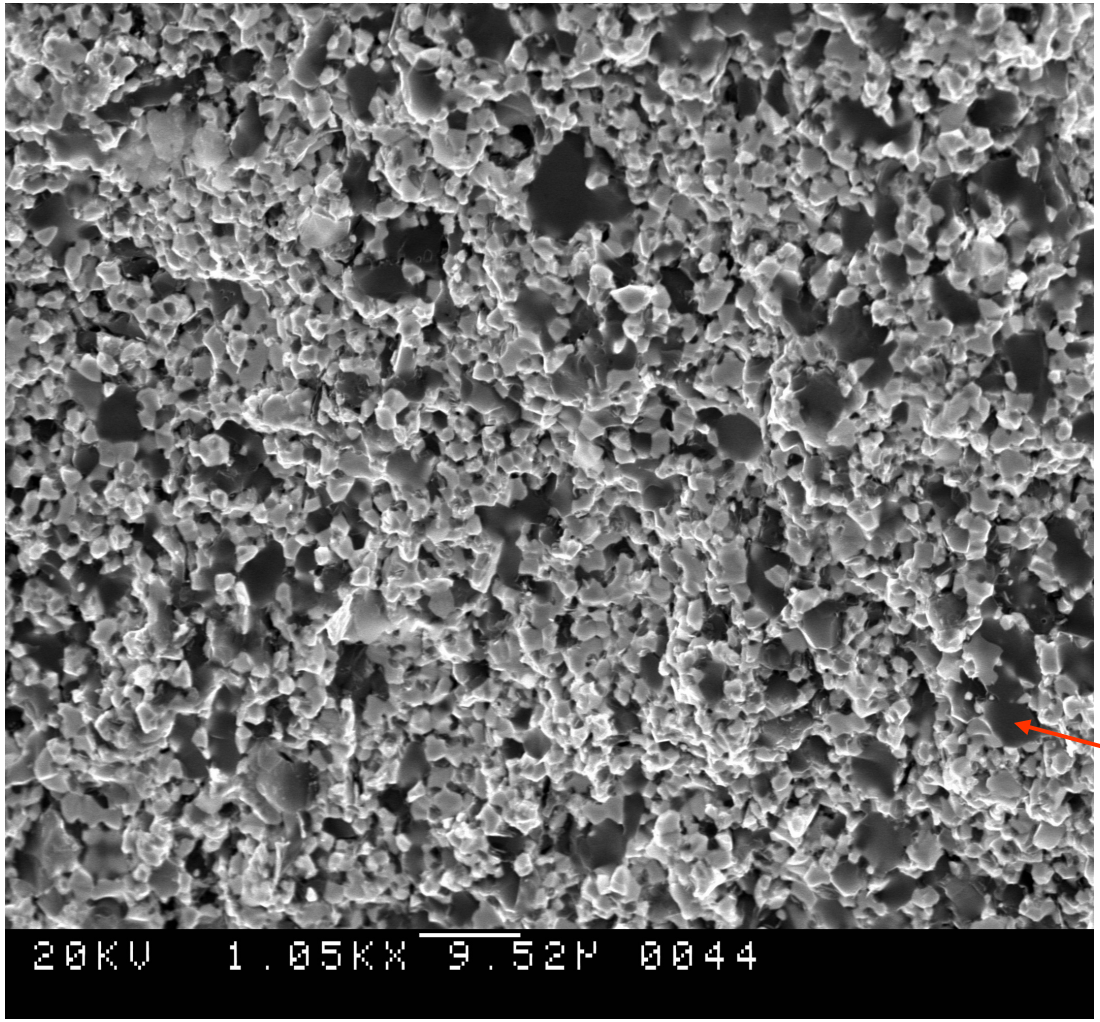
SEM of TaB_2 - C Ceramics Prepared from $TaC+B_4C$ Mixtures by Pressureless Reaction Sintering at 1900°C for 2 hours



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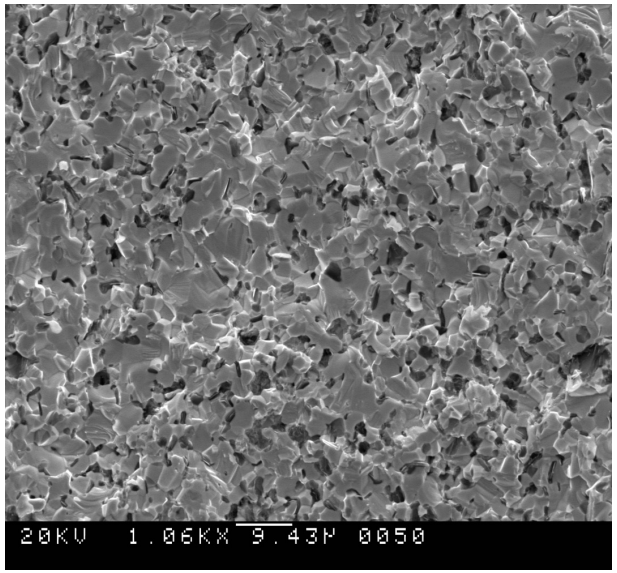
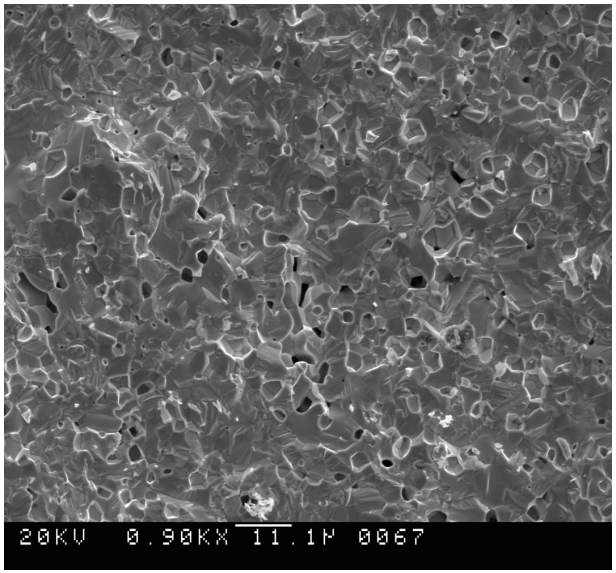
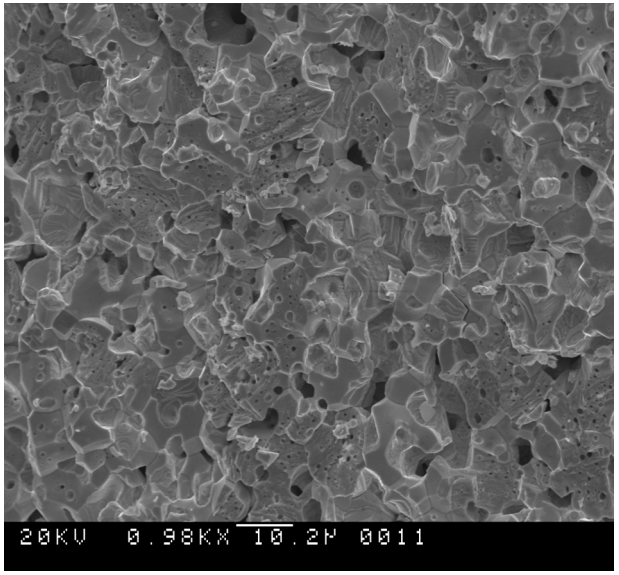
SEM of $TaC-TaB_2$ - C Ceramics Prepared from $TaC+B_4C$ Mixtures by Pressureless Sintering at 1900°C for 2 hours



4TaC



8TaC



12 TaC

Calculated Composition in vol.%

4:1, TaC – 35, TaB_2 – 42.5, C – 22.5

8:1, TaC – 62, TaB_2 – 25, C – 13

12:1, TaC – 73.8, TaB_2 – 17.6, C – 8.6

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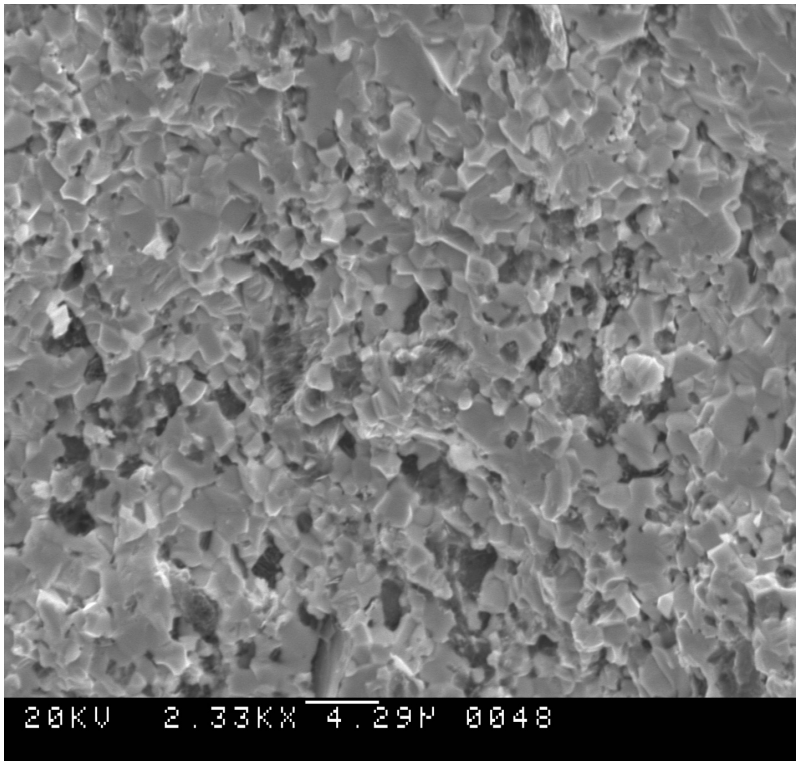
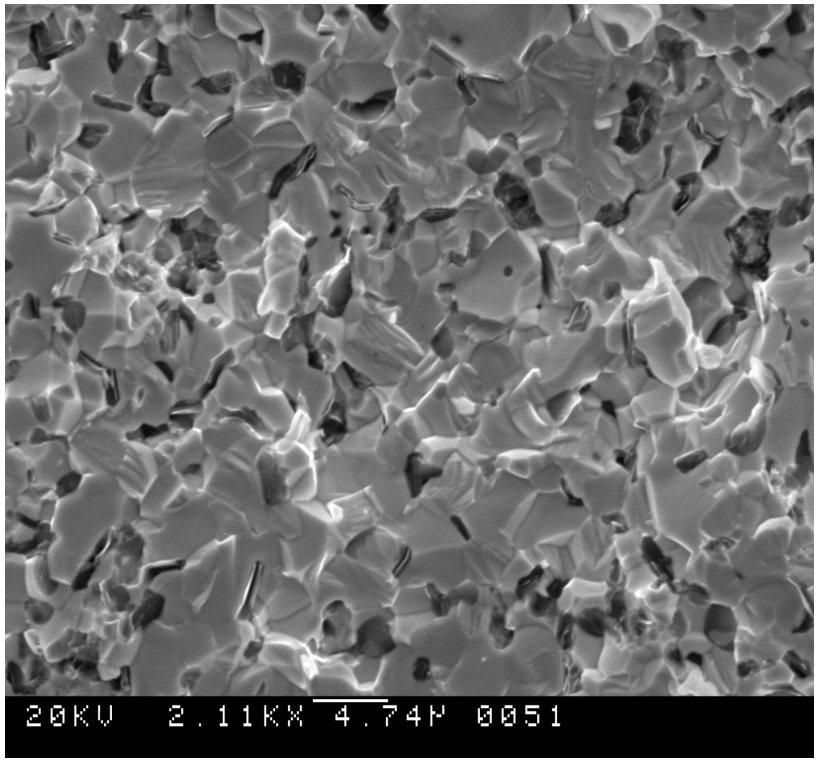
SEM of TaC-TaB_2 - C Ceramics Prepared from $4TaC+B_4C$ Mixture by Pressureless Sintering at 1700 and 1900°C for 2 hours

Calculated composition in vol. %: **TaC – 35, TaB_2 – 42.5, C – 22.5**



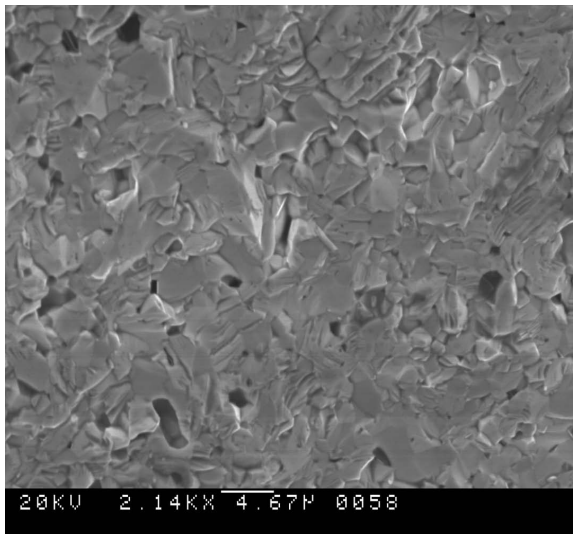
1700°C (Open porosity 3.1%)



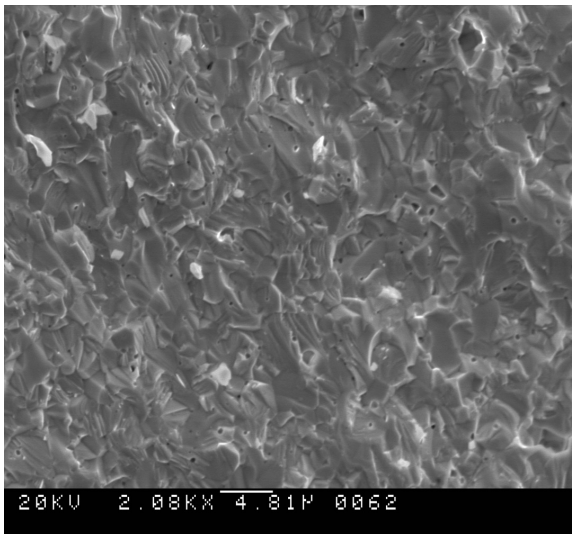
1900°C (Open porosity 0%)

SEM of TaC-TaB_2 - C Ceramics Prepared from 8TaC+B_4C Mixture by Pressureless Reaction Sintering

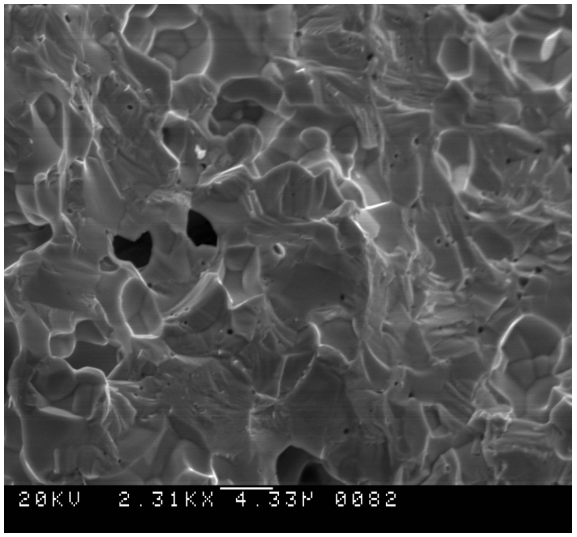
(TaC – 62, TaB_2 – 25, C – 13 vol. %)



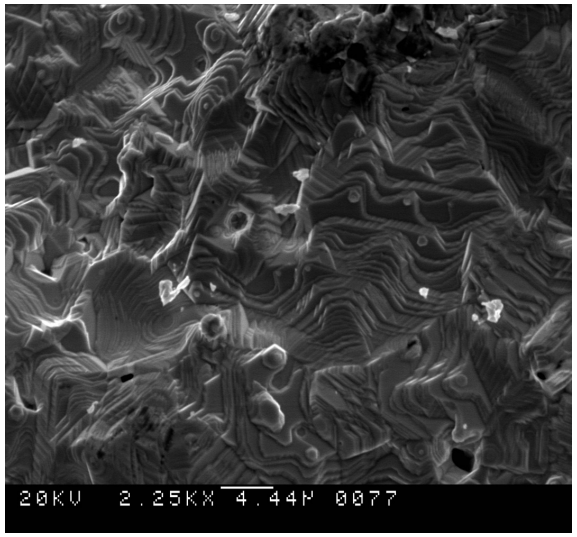
1700°C



1800°C



1900°C



2000°C, overfired

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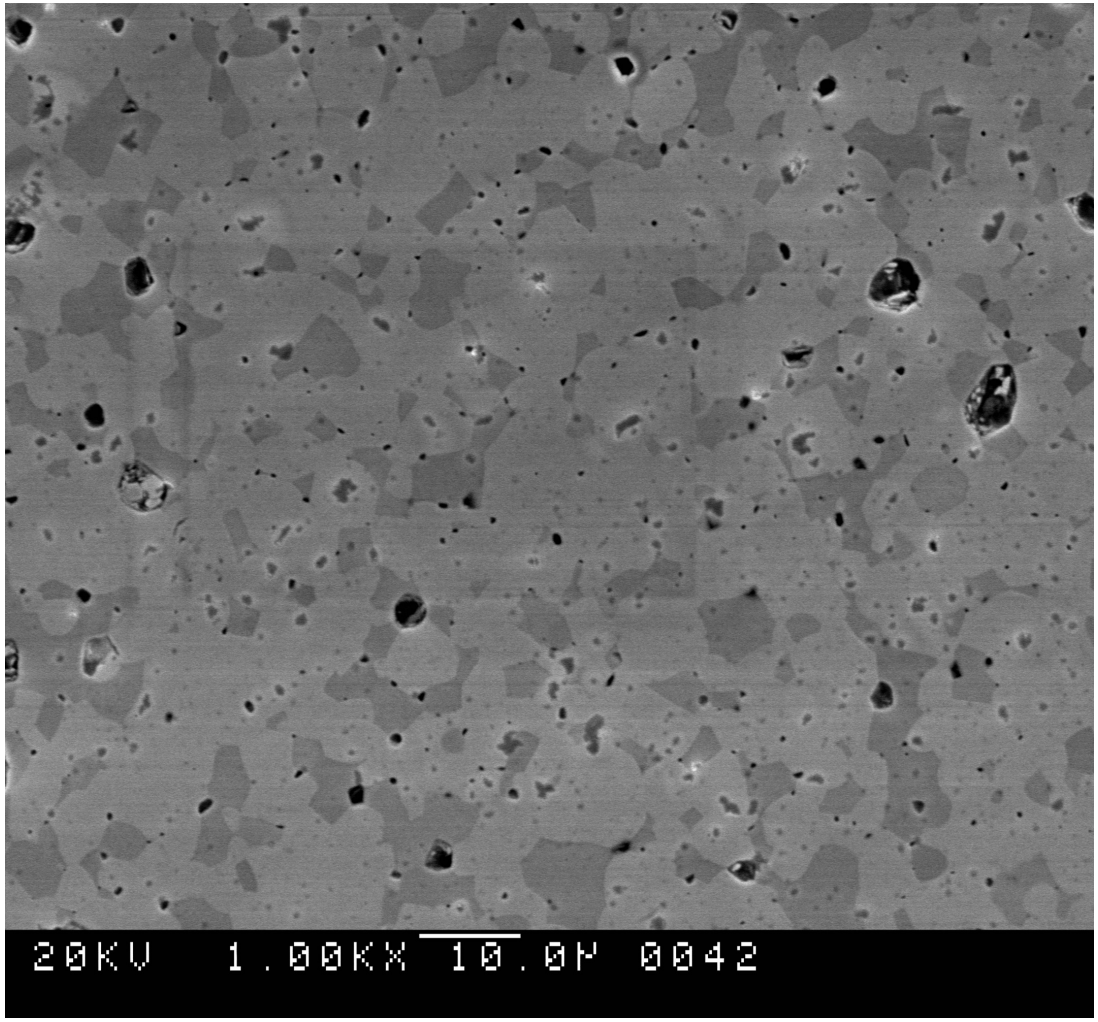
SEM of $TaC-TaB_2$ - C Ceramics Prepared from $8TaC+B_4C$ Mixture by Pressureless Reaction Sintering at 1900°C for 2 hours in He



Polished Surface

Composition in vol. %: **TaC – 62, TaB_2 – 25, C – 13**

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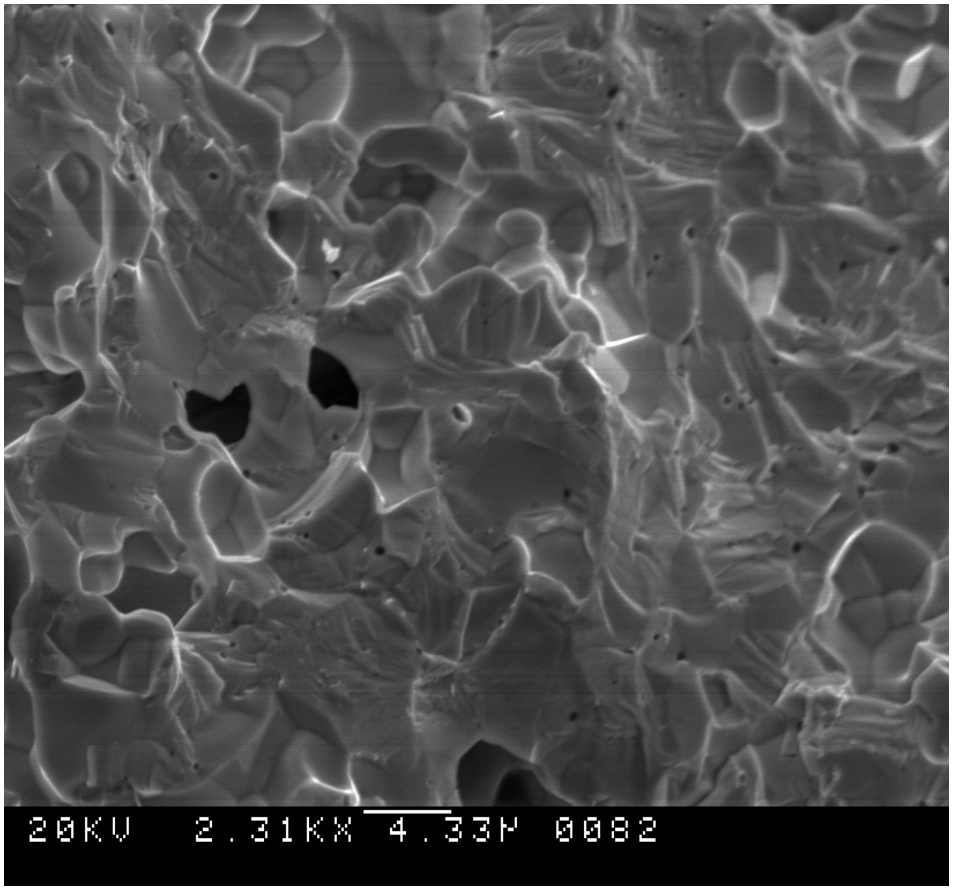
Mechanical Properties of 8TaC/B_4C (TaC–62, TaB_2–25, C – 13 vol. %) Ceramics Pressureless sintered at 1900°C



Flexural Strength (3-point)

221 MPa

Vickers Hardness

22.2 GPa

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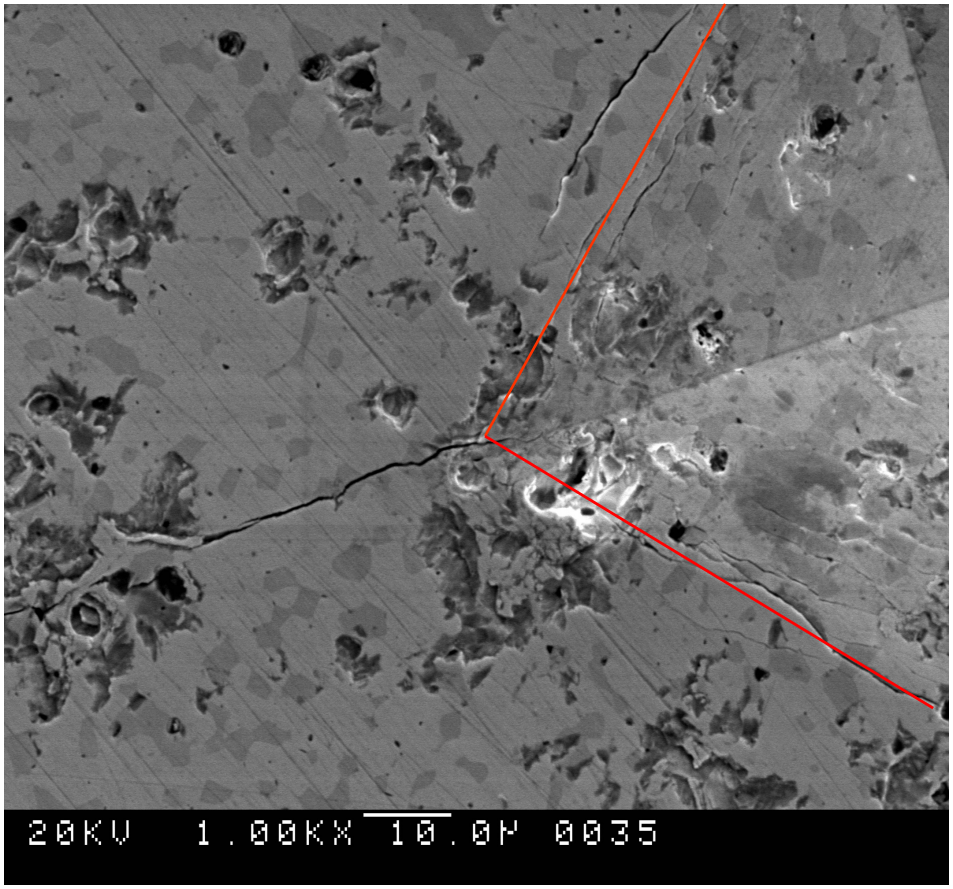
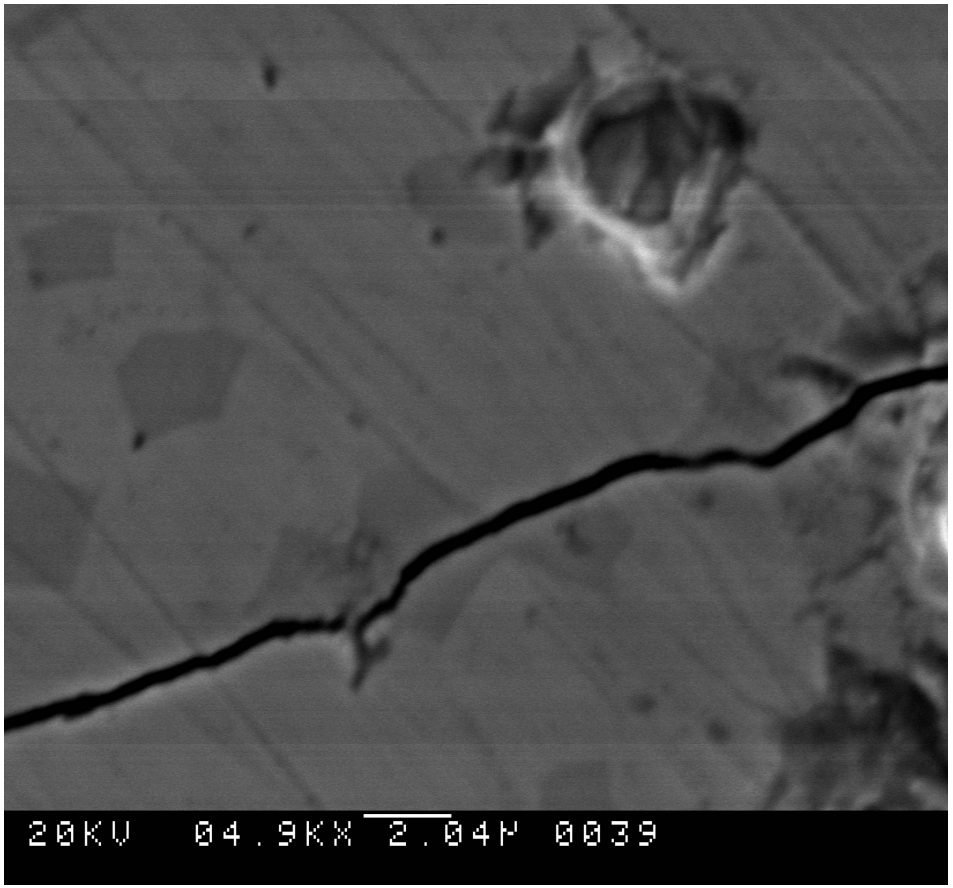
SEM of an Indent (10 kg load) in Ceramics from 8TaC+B_4C Mixture
Pressureless Sintered at 1900 C





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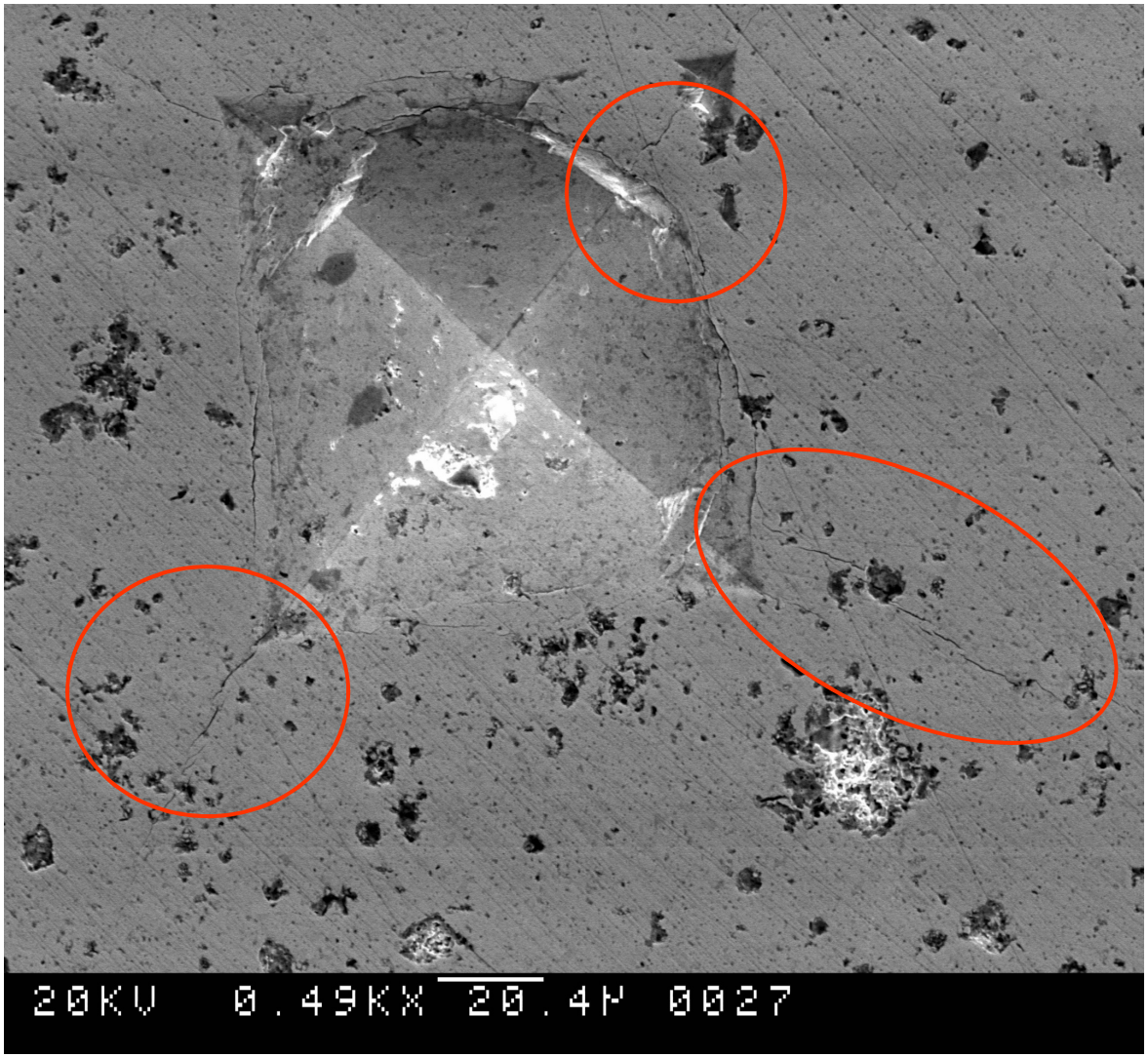
SEM of an Indent (10 kg load) in Ceramics from $12TaC+B_4C$ Mixture (TaC – 73.8, TaB_2 – 17.6, C – 8.6 vol. %) Hot Pressed at 1700 C



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Use of nano-TaC and nano-C black to Densify the End Members of the Reaction:

$$8TaC + B_4C \Rightarrow 6TaC + 2TaB_2 + 3C$$

- The end-member mixture was pressureless sintered to full density at 1850ºC (2 hours).

- The mixture of **nano TaC and TaB_2 (without carbon black) had open porosity of 19% after firing at 1800ºC** for 2 hours.

- The mixture of **6TaC, $2TaB_2$ and 3C** containing **coarse TaC (-325 mesh) and C black** had open porosity of 32.5% after pressureless firing at 2100ºC

Both sub-micron TaC and carbon black are needed for pressureless densification of TaC/TaB_2/C ceramics. **C black should be in the range of 2 to 8 wt. % of the TaC/Cmixture.**

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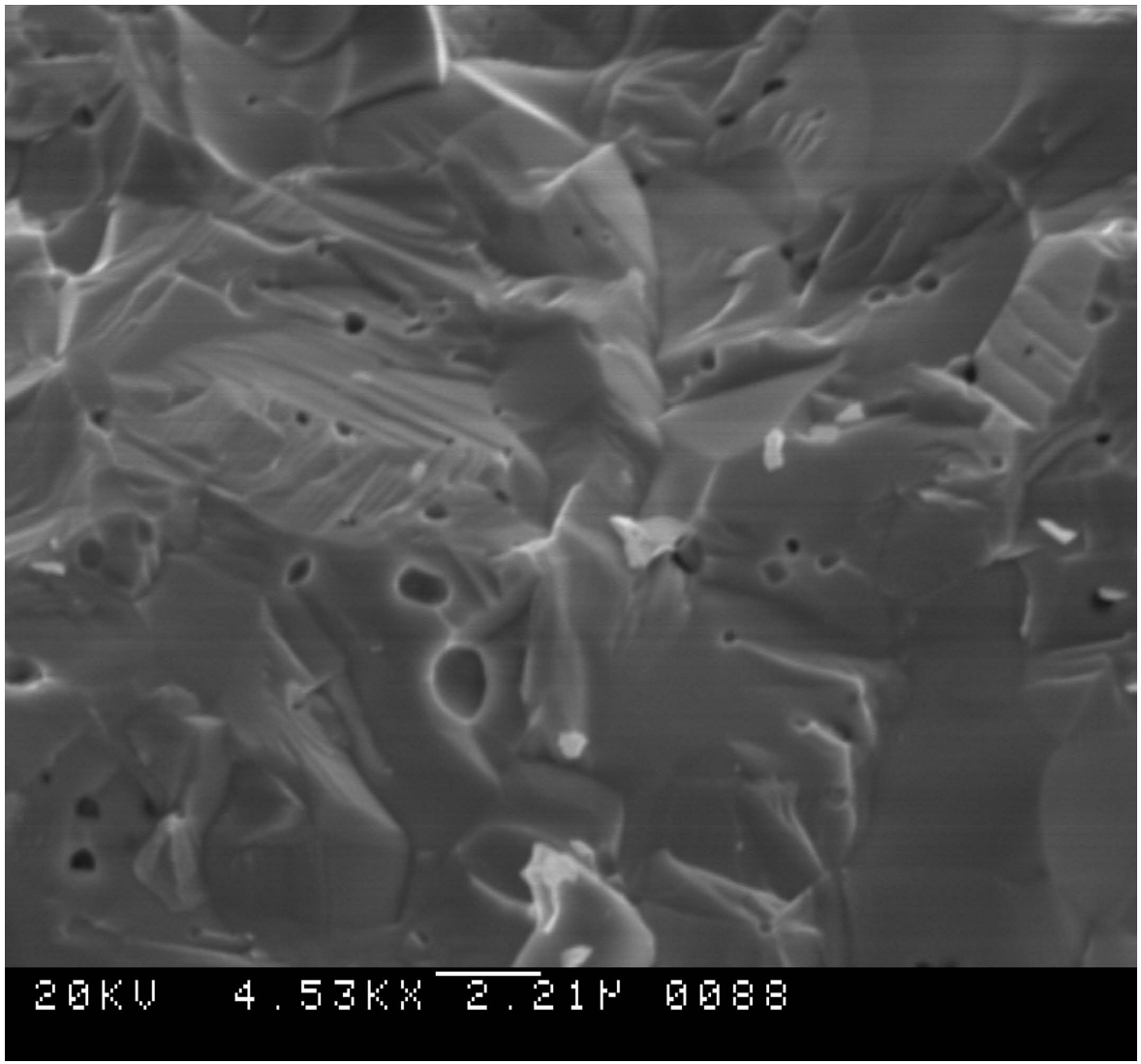
SEM of TaC-TaB_2 - C Ceramics Prepared from 6TaC + 2TaB_2+ 3C Mixture Pressurless Sintered at 1850°C



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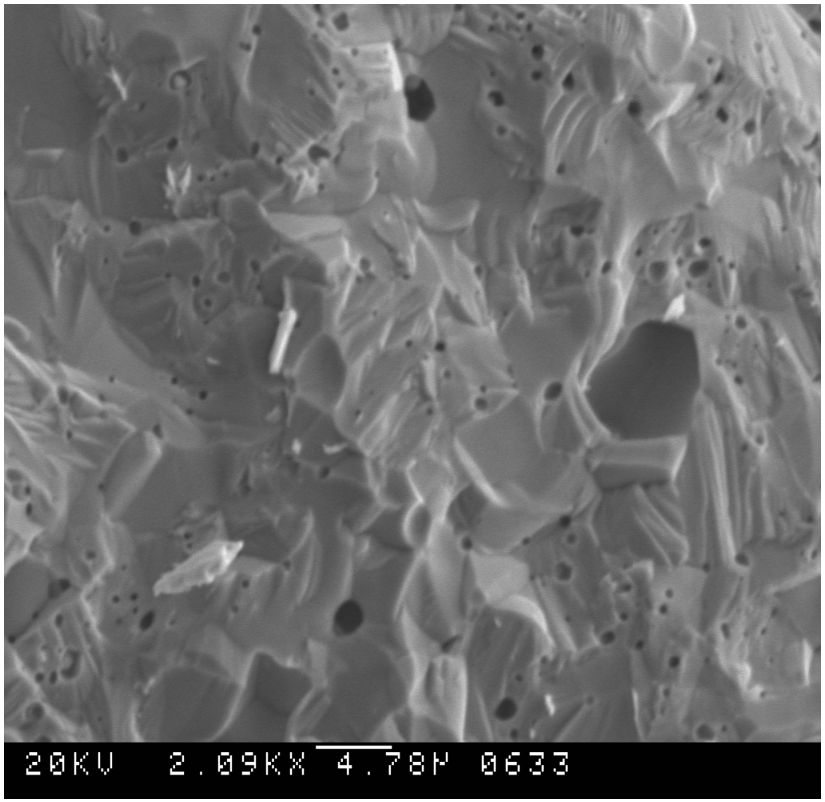
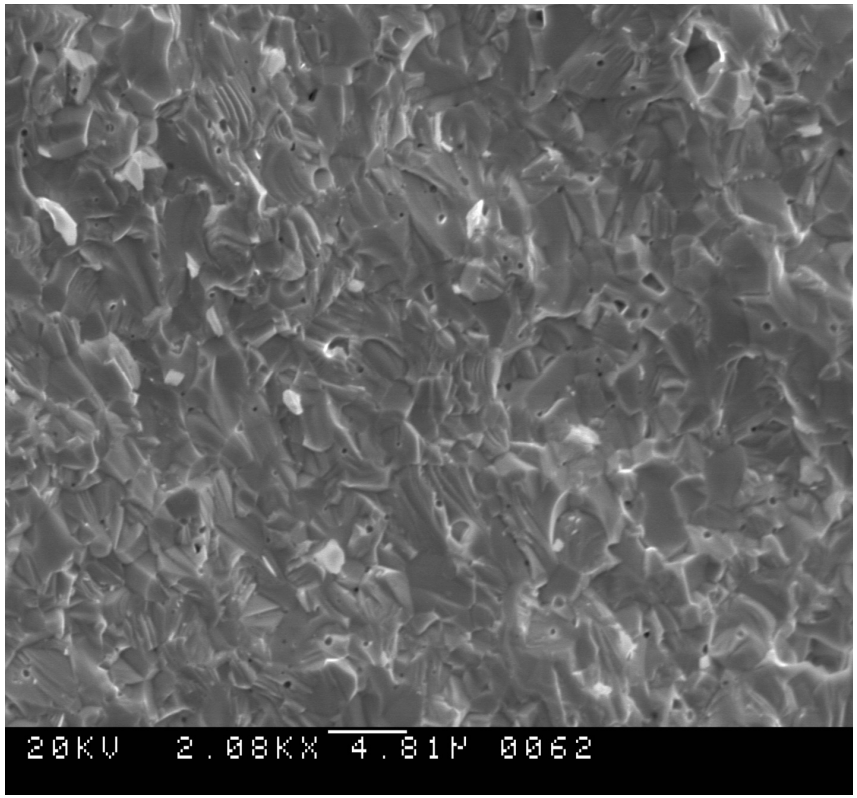
SEM of TaC-TaB_2 - C Ceramics Prepared from $8TaC+B_4C$ (reaction) and from $6TaC + 2TaB_2 + 3C$ (end members) Mixtures by Pressurless Sintering





$6TaC + 2TaB_2 + 3C$, 1850°C

Flexural Strength – 391 MPa

$8TaC+B_4C$, 1800°C

Flexural Strength – 221 MPa

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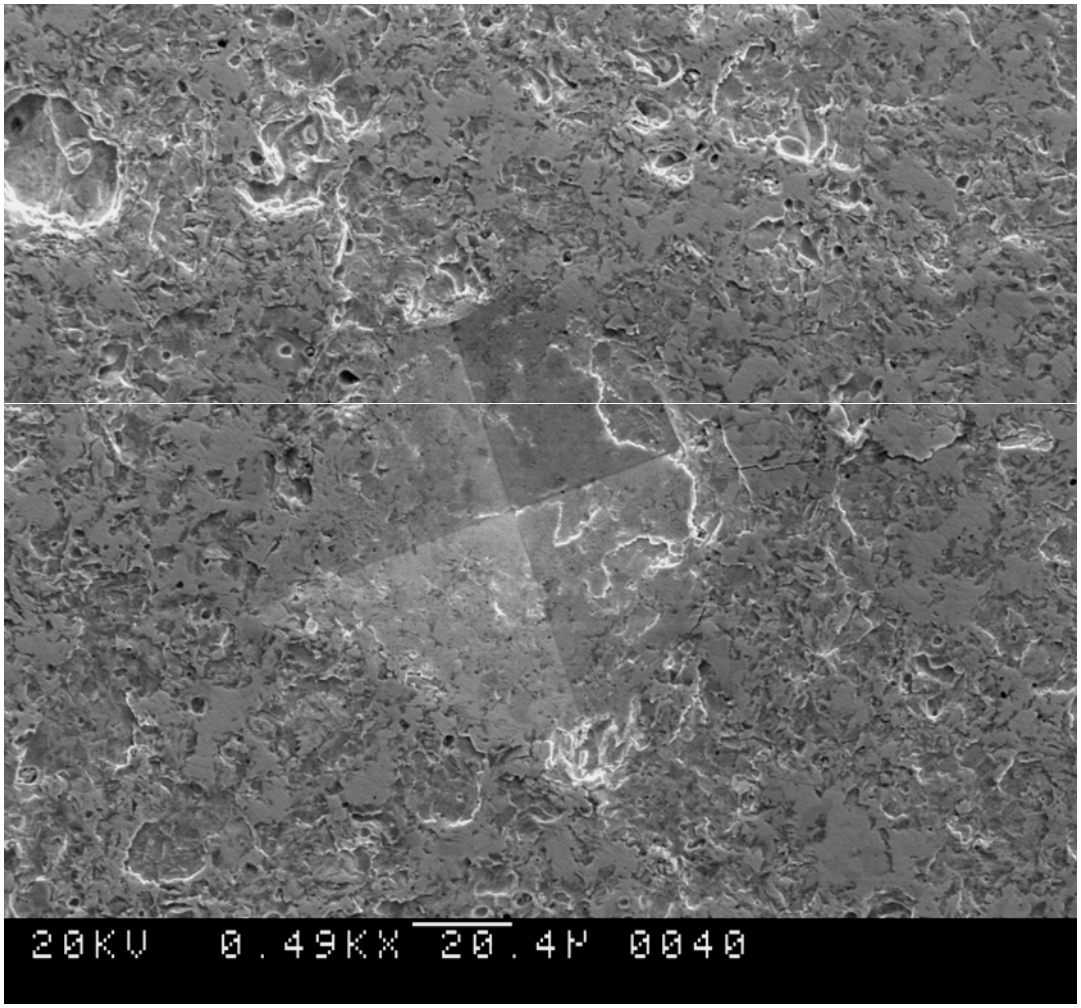
SEM of an Indent (10 kg load) in Ceramics from 6TaC + 2TaB_2+ 3C (end members) Mixture Pressurless Sintered at 1850°C



Hot Pressing Experiments

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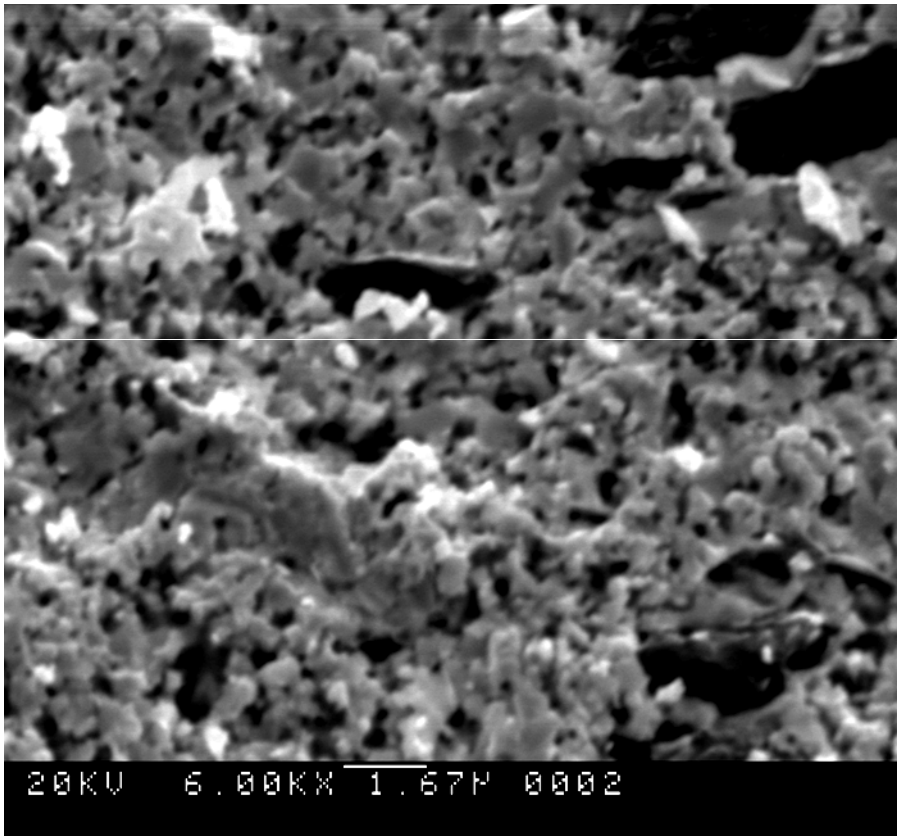
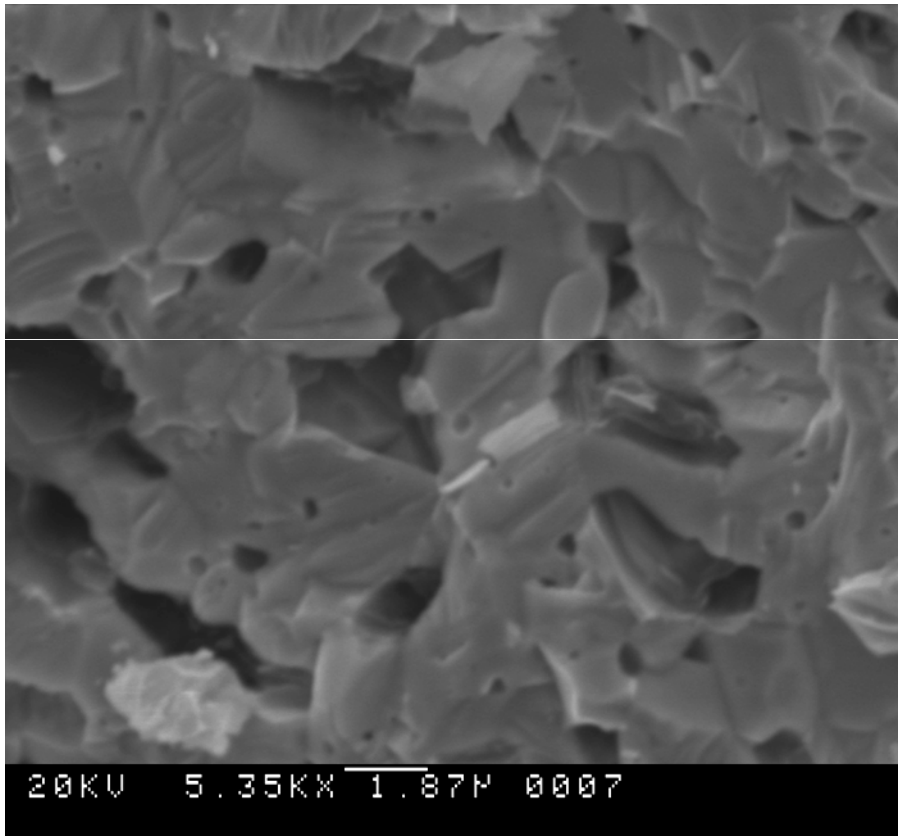
SEM of $TaC-TaB_2$ - C Ceramics Prepared from $8TaC+B_4C$ Mixture by Reaction Hot Pressing at 1700 and 1900°C for 1 hours in Ar



1700°C



1900°C

Open porosity about 12%

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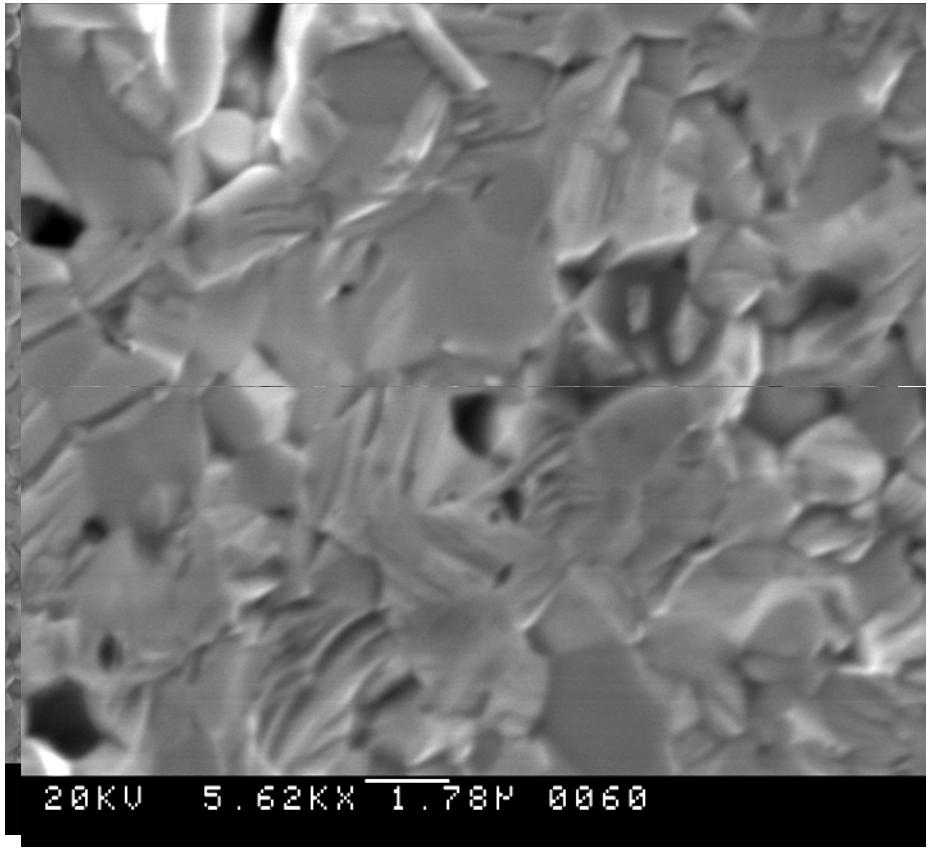
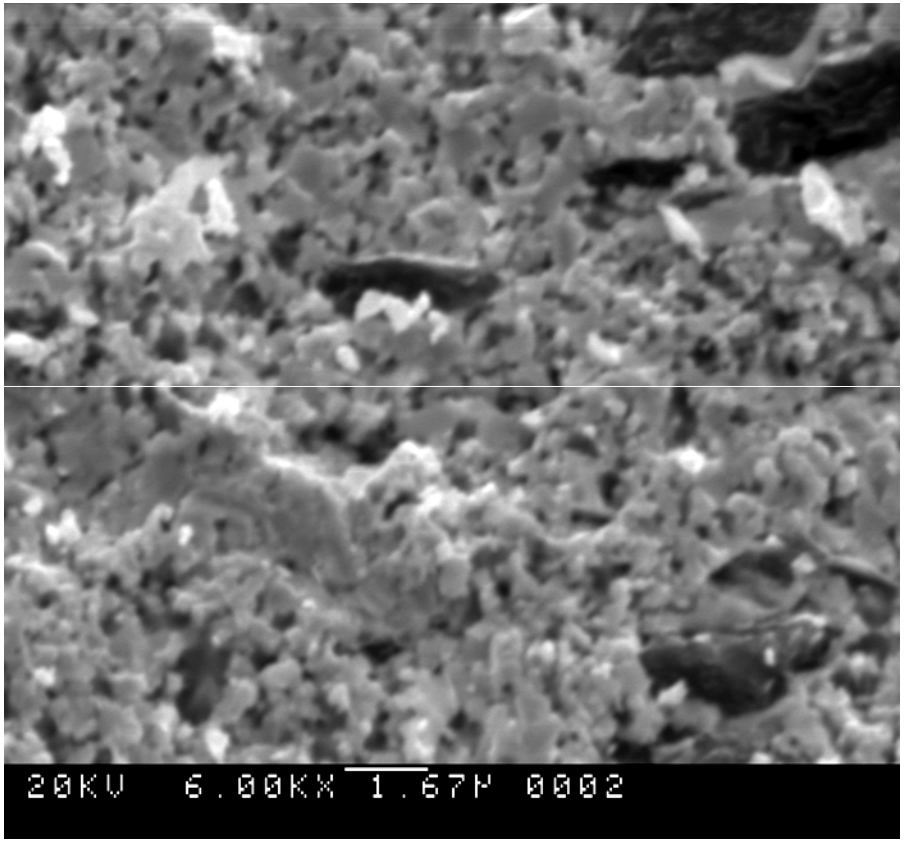
SEM of $TaC-TaB_2$ - C Ceramics Prepared from $8TaC+B_4C$ Mixture by Reaction Pressureless Sintering and Hot Pressing at 1700 C



Pressureless Sintering

Open porosity 0.2%



Hot Pressing

Open porosity 12%

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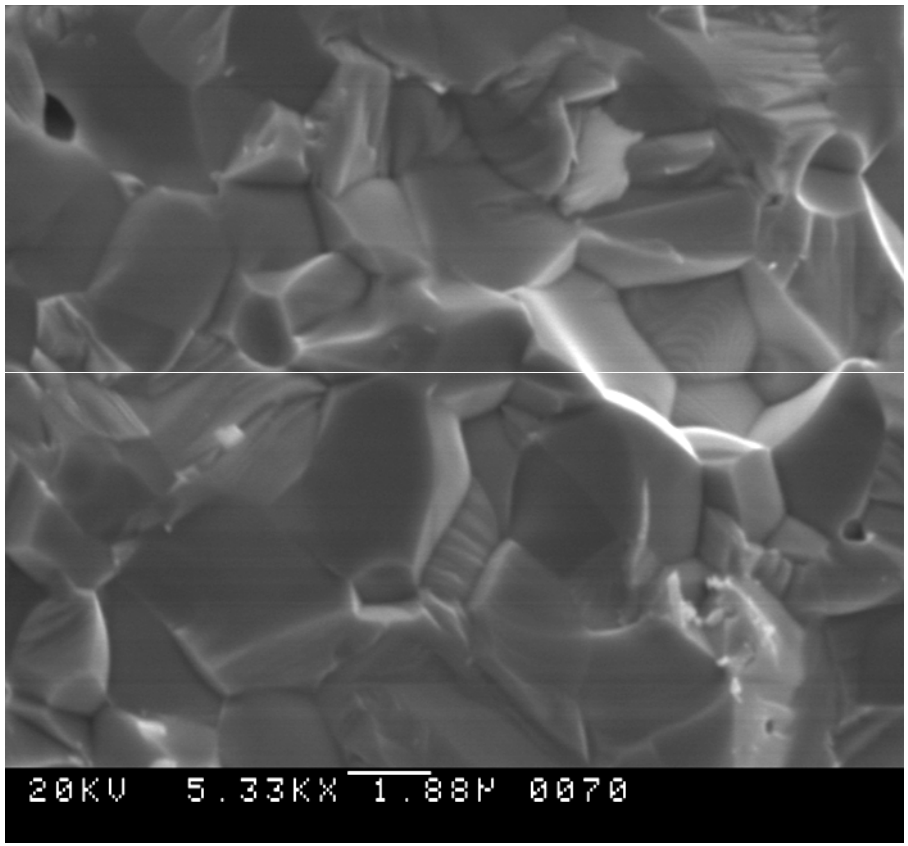
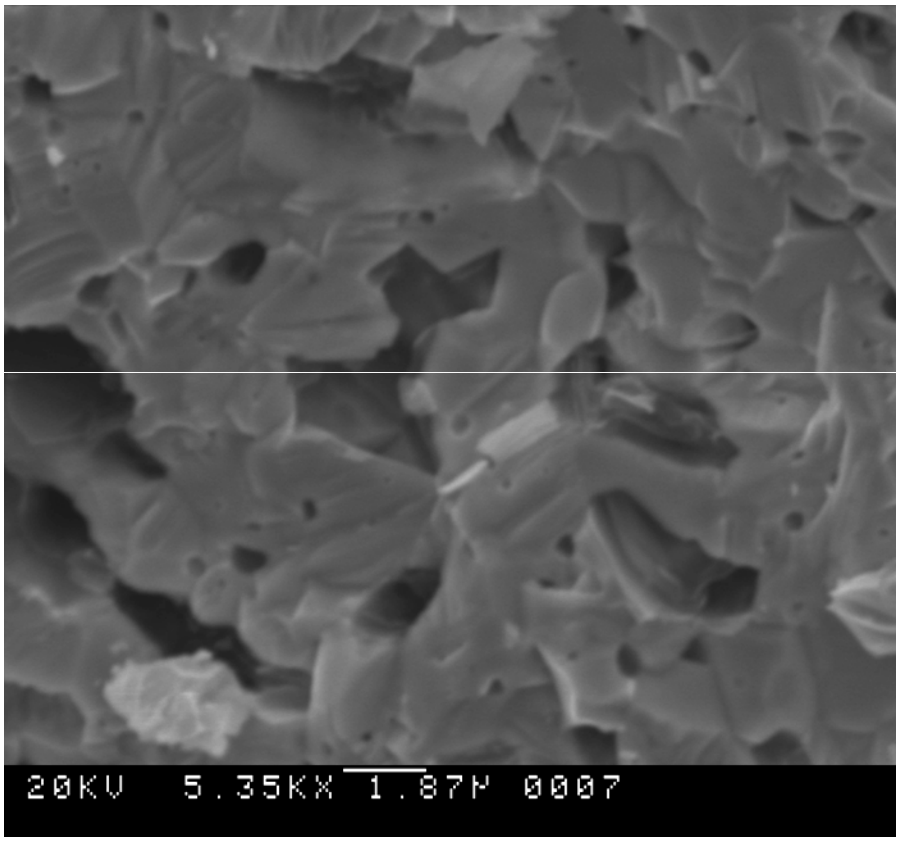
SEM of TaC-TaB_2 - C Ceramics Prepared from $8TaC+B_4C$ Mixture by Reaction Pressureless Sintering and Hot Pressing at 1900° C



Pressureless Sintering

Fully dense sample



Hot Pressing

Open porosity 12.5%

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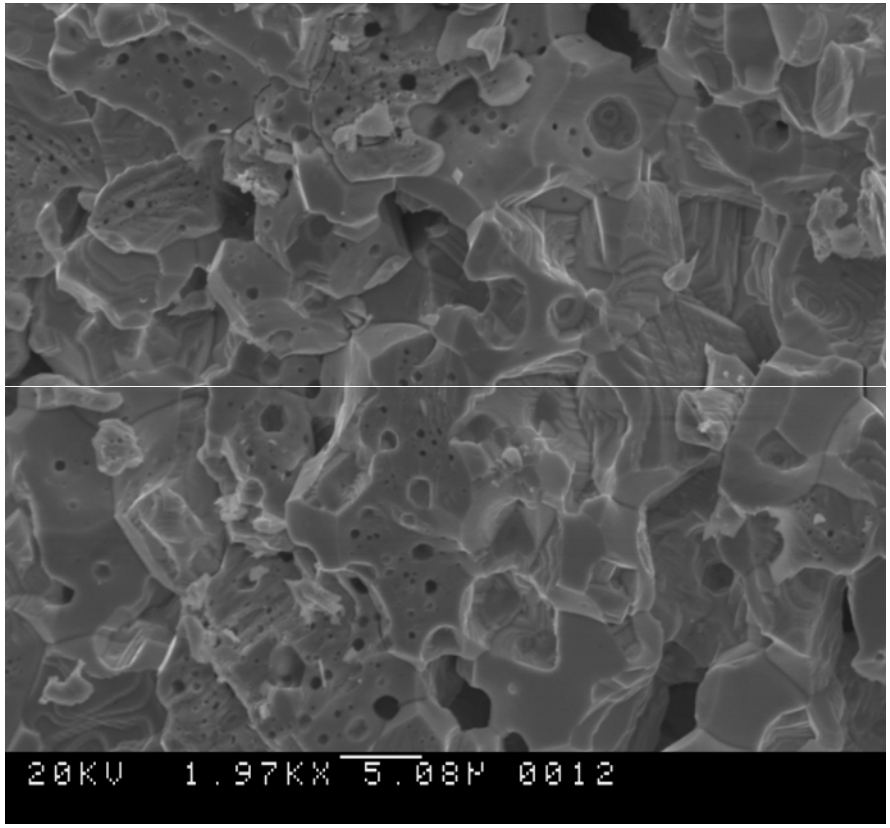
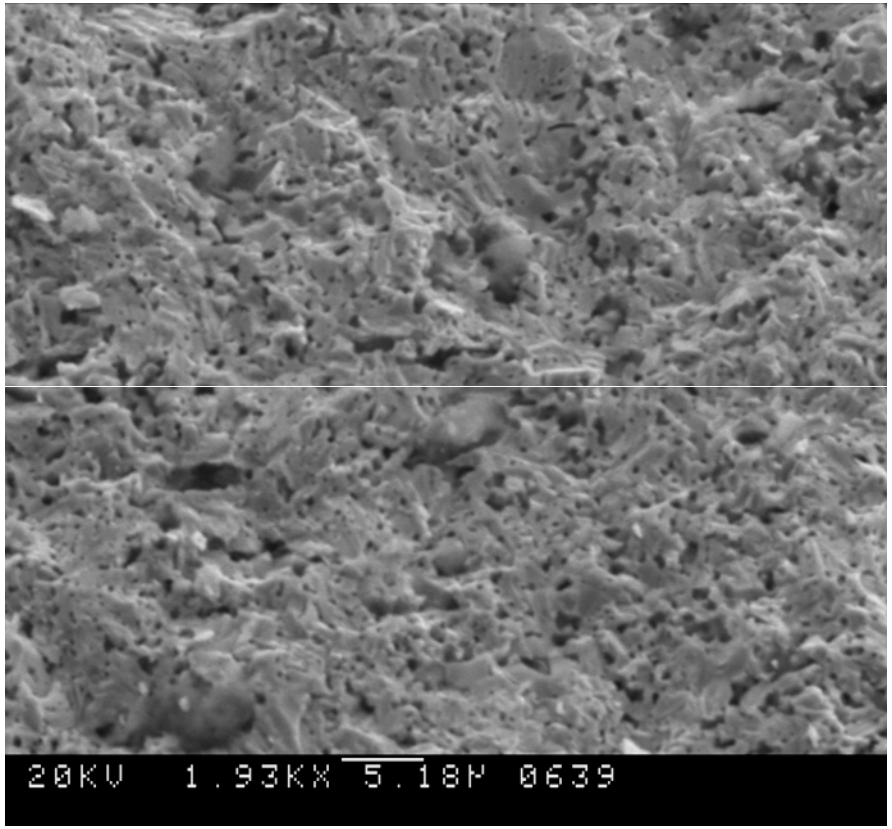
SEM of $TaC-TaB_2$ - C Ceramics Prepared from $12TaC+B_4C$ Mixture by Reaction Sintering and Hot Pressing



Pressureless at 1800°C for 2 hours

Open porosity 4.5%



HP at 1700°C for 1 hour

Open porosity 12.5%

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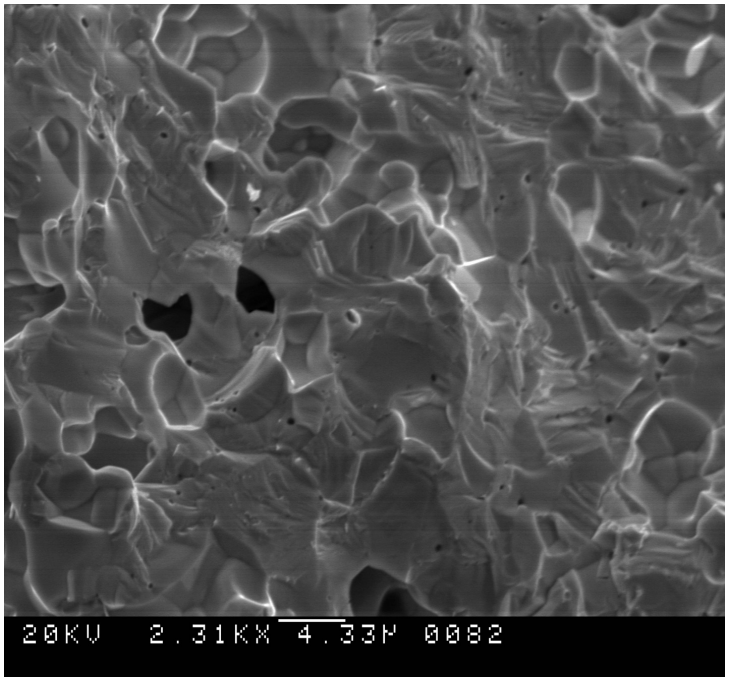
SEM, Flexural Strength (3-point), and Vickers Hardness of Ceramics: 8TaC/B_4C (TaC – 62, TaB_2 – 25, C – 13 vol. %)

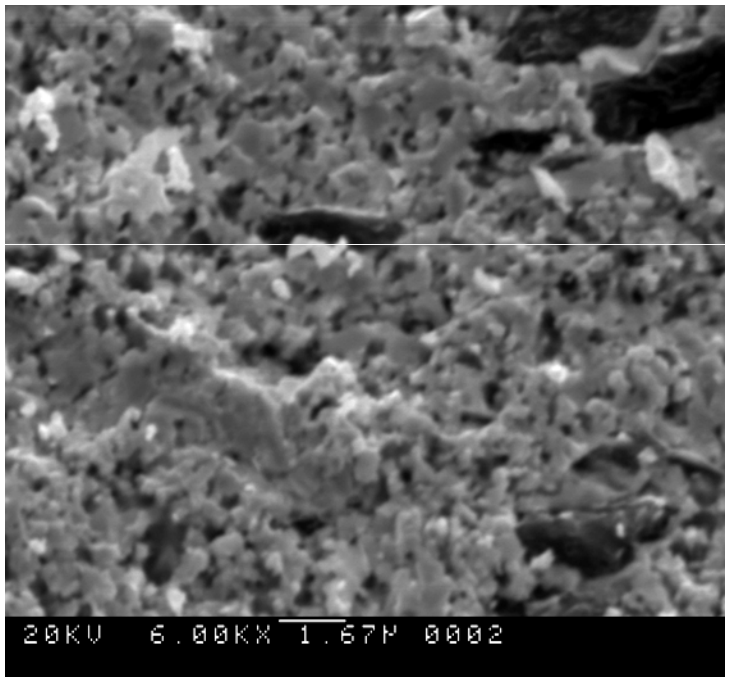
Pressureless sintered 1900°C



Strength-221 MPa

Hardness-22.2 GPa

Hot pressed 1700°C and 20MPa



Strength-293MPa

Hardness-8.2 GPa

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Summary

- Dense ceramics containing (in v.%) 35-73.8 TaC, 25-62 TaB_2, and 8.6-22.5 C were prepared by reactive pressureless sintering of sub-micron TaC with B_4C at 1700-1900°C.
- Reaction between TaC and B_4C was completed at about 1700°C.
- The densification of multi-phase ceramics was promoted by the formation of TaB_2 and active carbon. Carbon eliminated oxygen from the grain boundaries additionally enhancing sintering.
- Use of sub-micron TaC and carbon black together led to pressureless densification of non-reactive mixture of 6TaC, $2TaB_2$, 3C at 1850°C.
- The materials of all the tested compositions were not densified if a coarse TaC powder was used even in the presence of carbon black.
- Additional work is necessary to optimize processing parameters to remove oxygen at low temperatures, decrease shrinkage and stresses to increase the strength of ceramics.
- Low-temperature hot pressing is very promising for the development of high-strength multi-phase ceramics with a sub-micron grain size.
- Based on the results of this work and considering high potential of TaC for UHT applications, it is important to develop feasible low-cost method to produce sub-micron TaC and other carbides.